

WO 02/50230 A1

Job No.: 1505-96746

WO0250230

Translated from German by the Ralph McElroy Translation Co.
910 West Avenue, Austin, Texas, 78701

INTERNATIONAL PATENT OFFICE
WORLD ORGANIZATION FOR INTELLECTUAL PROPERTY

International patent published on
the basis of the Patent Cooperation Treaty (PCT)
INTERNATIONAL PUBLICATION NO. WO 02/50230 A1

International Patent Classification ⁷ :	C 11 D 3/50 A 61 K 7/46 A 61 L 9/01
International Filing No.:	PCT/EP01/14639
International Filing Date:	December 13, 2001
International Publication Date:	June 27, 2002
Priority	
Date:	December 20, 2000
Country:	DE
No.:	100 63 428.1
Language of Submission:	German
Language of Publication:	German

DISPERSIONS OF NANOPARTICULATE FRAGRANCE-CONTAINING COMPOSITE
MATERIALS

Inventors; and Inventors/Applicants (only for US):	Marcel Roth [DE/DE] Am Nettches Feld 21 40589 Düsseldorf (DE)
	Christian Knopf [DE/DE] Cäcilienstrasse 4 40597 Düsseldorf (DE)
	Christine Schröder [DE/DE] Am Alten Rhein 28 40593 Düsseldorf (DE)

Applicant (for all Designated
States except US):

Henkel Kommanditgesellschaft auf
Aktien (DE/DE)
Henkelstrasse 67
40589 Düsseldorf (DE)

Agent:

Henkel Kommanditgesellschaft auf
Aktien (DE/DE)
Henkelstrasse 67
40191 Düsseldorf (DE)

Designated States (national):

AU, BG, BR, BY, CA, CN, CZ, DZ,
HU, ID, IL, IN, JP, KR, MX, NO,
NZ, PL, RO, RU, SG, SI, SK, UA,
US, UZ, VN, YU, ZA

Designated States (regional):

European Patent (AT, BE, CH, CY,
DE, DK, ES, FI, FR, GB, GR, IE, IT,
LU, MC, NL, PT, SE, TR)

Published

- With International Search Report.
- Publication will be repeated if changes to the claims are submitted before the end of the allotted period.

For an explanation of the two-letter codes and the other abbreviations, please refer to the explanations ("Guidance Notes on Codes and Abbreviations") at the start of each regular edition of the PCT Bulletin.

(57) Abstract: The invention relates to aqueous dispersions of nanoparticulate composite materials, comprising at least one fragrance and an organic support and the particles comprise a mean particle diameter in the range of 1 to 500 nm. The fragrances contained in the composite materials are slowly released. The composite materials are thus preferably suitable for long-term perfuming of substrates, in particular textiles and keratin fibres.

The invention concerns aqueous dispersions of nanoparticulate composite materials, where the composite materials consist of at least one fragrance and an organic carrier and the particles have an average particle diameter in the range of 1-500 nm. The fragrances contained in the composite materials are slowly released from them. The composite materials are suitable for perfuming substrates, in particular textiles and keratin fibers.

Fragrances, also called odorants, have long been used, for example in washing agents, rinsing agents,* cleaning agents or finishing agents, as well as in cosmetic preparations. They are

* [Translator's note: This category includes agents for machine and hand dishwashing.]

currently not used so much to cover up the unpleasant characteristic odors of components contained in the said agents or preparations as in earlier times, but rather they are mainly used to give both the products themselves as well as objects or surfaces treated with the agents, or the body or parts of the body treated with the preparations, an odor that is pleasant and as long lasting as possible after the treatment. Moreover, a product identification is also achieved in the user via the odor of the product or the odor transferred to the treated object by the product; utilization of the odor in advertisements makes use of this product identification and is employed to promote sales. With finishing agents a special place is given to the fragrance in advertising and thus it is important in the consumer's mind. As a consequent of this, both among the manufacturers of washing, rinsing, cleaning or finishing agents and also among the manufacturers of cosmetic preparations, there is a demand for a way on the one hand to affix fragrances onto objects treated with such agents and thereby to allow the fragrances to be able to be released during or after treatment and on the other hand to lengthen the time for the release of the fragrances after treatment, as well.

The controlled release of fragrances in quite varied preparations of the washing, rinse, cleaning and body care sector, the so-called "slow release," is the subject of numerous publications and patent applications. This reflects that in this industrial field the release of fragrances is of prominent importance, since—for the reasons given above—both the product as well as the washing, rinsing, cleaning or finishing agent solutions and the objects treated with these agents are supposed to be perfumed intensively and lastingly. Besides the methods of applying fragrances to carrier materials and then coating these materials or encapsulating fragrances or putting them in a complex compound (for example cyclodextrin-fragrance complexes), there is the possibility of binding the fragrances chemically to carriers, where the chemical binding breaks down slowly and the fragrance is released. This principle was realized, for example, in the esterification of fragrance alcohols, as described in the publication WO 97/30687. The prior Patent Application DE 198 41 147.2 (Henkel KGaA) discloses esters of oligosilicic acids with fragrance alcohols that enable long-lasting perfuming of objects (including the human body or parts of the human body such as the hair). However, problems arise when the said compounds of the prior art are used in washing and cleaning agents and also in cosmetic preparations. For instance, many of the known compounds cannot be used in aqueous washing and cleaning agents, since they hydrolyze in the product and, because of this, the subsequent delayed release no longer takes place. This is even more the case since the conventional cleaning and washing agents frequently have pH values that favor the hydrolysis of fragrance esters. Another disadvantage of the approaches of the prior art lies in the frequently only limited capacity of the controlled release fragrance formulations to be incorporated into preparations,

especially ones with a high water content. This rather leads to instability of the preparations, for example in the form of phase separations and sedimentation phenomena. Furthermore, in many cases the accompanying substances that are incorporated into preparations along with the controlled release fragrance formulations are undesirable, for example alcohols as the hydrolysis product of the above-mentioned fragrant esters, or cyclodextrins in the case of fragrance-cyclodextrin complexes.

Thus, there was additionally a need to make available industrially readily accessible, cheap and widely usable fragrance forms that are especially suitable for use in washing, cleaning or finishing agents or cosmetic preparations and that give the objects treated with these agents a long lasting odor. The task of the invention was also to make available methods for washing, rinsing, cleaning or finishing and also for cosmetic treatment of the body with which a long lasting fragrance can be applied to the material that is washed, rinsed or cleaned or the human body or parts of the human body.

It was surprisingly now found that the odor of preparations of the most varied kinds, for example washing agents, rinsing agents, cleaning agents, finishing agents, or even of cosmetic preparations, can be transferred to objects treated with these preparations and released from them over a long period of time, if the relative preparations contain a nanoparticulate aqueous dispersion of a composite material made of an organic carrier and at least one fragrance.

The invention therefore concerns an aqueous dispersion of a nanoparticulate composite material, where the composite material consists of at least one fragrance and an organic carrier and the particles have an average particle diameter in the range of 1-500 nm and preferably in the range of 10-200 nm.

The sizes are to be understood as diameters in the direction of the greatest linear extension of the particles. In the preparation of the particles one always obtains particles with a size that follows a distribution curve. For experimental determination of the particle size one can use, for example, the methods of dynamic light scattering that are known to the specialist.

As fragrances, also called odorants, it is possible to use, for example, compounds from the classes of the esters, ethers, aldehydes, ketones, alcohols or hydrocarbons. Fragrances of the ester type are, for example, benzyl acetate, phenoxyethyl isobutyrate, p-tert-butylcyclohexyl acetate, linalyl acetate, dimethylbenzylcarbinyl acetate (DMBCA), phenyl ethyl acetate, benzyl acetate, ethylmethylphenyl glycinate, allylcyclohexyl propionate, styryl propionate, benzyl salicylate, cyclohexyl salicylate, floramate, melusate and jasmacylate. Among the ethers are, for example, benzyl ether ether and ambroxan, the aldehydes include, for example, the linear alkanals with 8-18 C atoms, citral, citronellal, citronellyloxy acetaldehyde, cyclamenaldehyde, linal and bourgeonal, the ketones include, for example, the ionones, α -isomethylionone and

methyl cedryl ketone, the alcohols include anethol, citronellol, eugenol, geraniol, linalool, phenyl ethyl alcohol and terpineol, while the hydrocarbons include mainly the terpenes like limonene and pinene.

However, preferably mixtures of different fragrances that together produce a pleasant odor note are used. Such mixtures are also called perfume oils when they are in liquid form at room temperature.

As fragrances or fragrance mixtures it is also possible to use natural products from plant sources, for example pine, citrus, jasmine, patchouli, rose or ylang-ylang oil. Likewise suitable are clary sage oil, chamomile oil, clove oil, balm oil, mint oil, cinnamon oil, basswood oil, juniper berry oil, vetiver oil, olibanum oil, galabanum oil and labdanum oil as well as orange blossom oil, neroli oil, orange peel oil and sandalwood oil.

To be perceptible, a fragrance must be volatile, and molecular weight also plays an important role in addition to the nature of the functional groups and the structure of the chemical compound. Thus, most fragrances have molecular weights up to about 300 daltons, with higher molecular weights rather being an exception. Because of the different volatilities of fragrances the odor of a perfume or fragrance composed of several fragrances changes during evaporation, the impressions of odor being divided into "top note," "middle note" or "body" and "end note" or "dry out." Since the perception of odor to a large extent also stems from the intensity of the odor, the top note of a perfume or fragrance does not consist solely of readily volatile compounds, while the end note for the most part consists of less volatile, i.e., clingy fragrances. In the composition of a perfume more volatile fragrances can be bonded, for example, to certain fixatives, so that evaporation that is too rapid is prevented. Therefore, in the following distribution of fragrances into "more volatile" or "clingy" fragrances nothing is said about the impression of odor or about whether the corresponding fragrance is perceived as a top note or middle note.

Clingy fragrances that can be used within the scope of this invention are, for example, the essential oils like angelica root oil, anise oil, arnica oil, basil oil, bay oil, champac flower oil, silver fir oil, silver fir cone oil, elemi oil, eucalyptus oil, fennel oil, spruce needle oil, galbanum oil, geranium oil, ginger grass oil, pockwood oil, gurjun balsam oil, helichrisum oil, ho oil, ginger oil, iris oil, cajaput oil, calimus oil, chamomile oil, camphor oil, canaga oil, cardamom oil, cassia oil, pine needle oil, copaiba balsam oil, coriander oil, curled mint oil, caraway oil, cumin oil, lavender oil, lemon grass oil, lime oil, tangerine oil, sweet balm oil, musk oil, myrrh oil, clove oil, neroli oil, niaouli oil, olibanum oil, oregano oil, palmarosa oil, patchouli oil, peru balsam oil, petigrain oil, pepper oil, peppermint oil, pimento oil, pine oil, rose oil, rosemary oil, sandalwood oil, celery oil, spike oil, star anise oil, turpentine oil, thuja oil, thyme oil, verbena oil,

vetiver oil, juniper berry oil, worm wood oil, wintergreen oil, ylang ylang oil, hyssop oil, cinnamon oil, cinnamon leaf oil, citronella oil, lemon oil and cypress oil. However, the higher-boiling or solid fragrances of natural or synthetic origin can also be used as clingy fragrances or fragrance mixtures within the scope of this invention. These compounds include the following compounds as well as mixtures of them: ambrettolide, ambroxan, α -amylcinamaldehyde, anethol, anisaldehyde, anise alcohol, anisole, anthranilic acid methyl ester, acetophenone, benzyl acetone, benzaldehyde, benzoic acid ethyl ester, benzophenone, benzyl alcohol, benzyl acetate, benzyl benzoate, benzyl formate, benzyl valerianate, borneol, bornyl acetate, boisambrene forte, α -bromosytrene, n-decyl aldehyde, n-dodecyl aldehyde, eugenol, eugenol methyl ether, eucalyptol, farnesol, fenchone, fenchyl acetate, geranyl acetate, geranyl formate, heliotropin, heptine carboxylic acid methyl ester, heptaldehyde, hydroquinone dimethyl ether, hydroxy cinamaldehyde, hydroxy cinnamic alcohol, indole, irone, isoeugenol, isoeugenol methyl ether, isosafrol, jasmon, camphor, carvacrol, carvone, p-cresol methyl ether, coumarin, p-methoxyacetophenone, methyl-n-amyl ketone, methyl anthranilic acid methyl ester, p-methyl acetophenone, methyl chavicol, p-methyl quinoline, methyl- β -naphthyl ketone, methyl-n-nonyl acetaldehyde, methyl n-nonyl ketone, muskone, β -naphthol ethyl ether, β -naphthol methyl ether, nerol, n-nonyl aldehyde, nonyl alcohol, n-octyl aldehyde, p-oxyacetophenone, pentadecanolide, β -phenyl ethyl alcohol, phenyl acetaldehyde dimethyl acetal, phenyl acetic acid, pulegon, safrol, salicylic acid isoamyl ester, salicylic acid methyl ester, salicylic acid hexyl ester, salicylic acid cyclohexyl ester, santalol, sandelice, skatole, terpeneol, thymine, thymol, troenane, γ -undelactone, vanilin, veratrum aldehyde, cinnamaldehyde, cinnamic alcohol, cinnamic acid, cinnamic acid ethyl ester, cinnamic acid benzyl ester.

The more volatile fragrances include, in particular, the low-boiling fragrances of natural or synthetic origin, which can be used by themselves or in mixtures. Examples of more volatile fragrances are diphenyl oxide, limonene, linalool, linalyl acetate and propionate, melusate, menthol, menthone, methyl-n-heptenone, pinene, phenyl acetaldehyde, terpinyl acetate, citral, citronellal.

In accordance with the invention a single fragrance or mixtures of different fragrances can be used. Fragrance mixtures are preferred, especially perfume oils.

Suitable as organic carrier in the sense of the invention are, for example, waxes, higher fatty alcohols, fatty alcohol alkoxylates, fatty acid amides, quaternary ammonium compounds and quaternary phosphonium compounds, insofar as these have a melting point of more than 40°C and are sparingly soluble in water. In the sense of the invention a solubility of less than 5 wt%, preferably less than 1 wt%, with respect to the total weight of the solution, is to be understood under the term sparingly soluble.

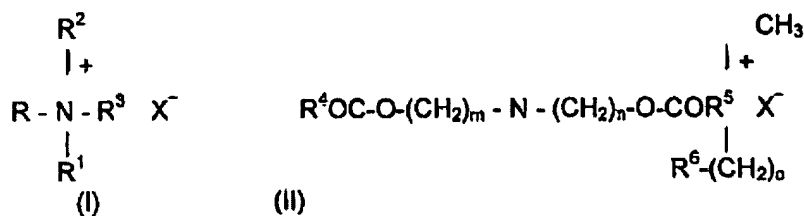
Waxes in the sense of the invention are understood to mean natural or synthetic substances that at 20°C are kneadable, solid to brittle, coarse to finely crystalline, translucent to opaque, but are not glass-like, that melt without decomposing above about 40°C and a little above the melting point already have low viscosity and do not become stringy. The waxes that are to be used in the sense of the invention differ, for example, from resins in that they pass into the molten, low-viscosity state and are practically free of ash-forming compounds between about 50 and 90°C as a rule, and in exceptional cases up to 200°C. According to origin the waxes are divided into the following three groups: natural waxes of plant or animal origin, for example, candelilla wax, carnauba wax, Japan wax, esparto grass wax, cork wax, guaruma wax, rice germ oil wax, sugar cane wax, ouricury wax, montan wax, beeswax, shellac wax, spermaceti, lanolin (wool wax), tail wax, ceresine, ozokerite (mineral wax), petrolatum, paraffin waxes, microwaxes, chemically modified waxes (hard waxes) such as montan ester waxes, sasol waxes, hydrogenated jojoba waxes or hydrogenated castor oil, as well as synthetic waxes such as polyalkylene waxes and polyethylene glycol waxes.

Higher fatty alcohols are understood to be primary aliphatic alcohols of the formula R-OH, in which R stands for an aliphatic, linear or branched hydrocarbon residue with 14-40 carbon atoms and 0, 1, 2 or 3 double bonds. Typical examples are myristyl alcohol, cetyl alcohol, palmoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, linolyl alcohol, linolenyl alcohol, elaeostearyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol, brassidyl alcohol, lignoceryl alcohol, ceryl alcohol, myricyl alcohol, melissyl alcohol and their mixtures. The fatty alcohols can be of vegetable, animal or synthetic origin.

Synthetic fatty alcohol mixtures that can be used in accordance with the invention are obtained from industrial methyl esters based on fats and oils or aldehydes from the Roelen oxosynthesis and as monomer fraction in the dimerization of unsaturated fatty alcohols. Higher fatty alcohols of plant origin, especially preferably ones with 16-18 carbon atoms, are preferred. Further preferred is cetylstearyl alcohol, which is understood to mean mixtures of approximately equal amounts of acetyl and stearyl alcohol.

Fatty alcohol alkoxylates that are suitable in accordance with the invention are addition products at 2-100 mol ethylene oxide and/or 0-20 mol propylene oxide to linear fatty alcohols with 8-22 C atoms.

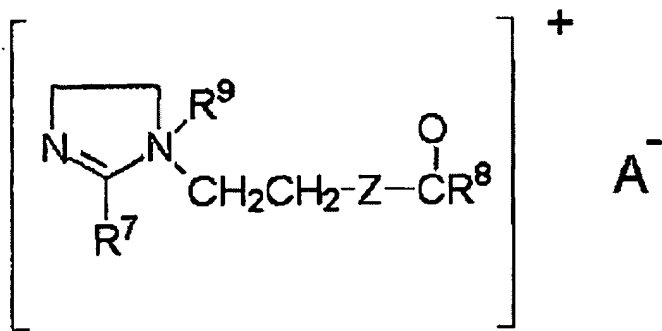
Quaternary ammonium compounds in the sense of the invention are understood to mean, for example, quaternary ammonium compounds of formulas (I) and (II),



in which R and R¹ stand for an acyclic alkyl residue with 12-24 carbon atoms, R² stands for a saturated C₁-C₄ alkyl or hydroxyalkyl residue, R³ is either the same as R, R¹ or R², and COR⁴ and COR⁵ in each case stand for an aliphatic acyl residue with 12-22 carbon atoms with 0, 1, 2 or 3 double bonds, and R⁶ stands for H or OH, where m, n and o, in each case independent of one another, can have the value 1, 2 or 3 and X is either a halide, methosulfate, methophosphate or phosphate ion, as well as mixtures of these compounds. Compounds that contain alkyl residues with 16-18 carbon atoms are especially preferred.

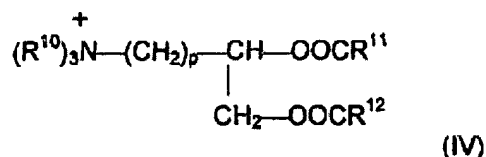
Examples of cationic compounds of formula (I) are didecyldimethylammonium chloride, ditallow dimethylammonium chloride or dihexadecylammonium chloride. Examples of compounds of formula (II) are methyl-N-(2-hydroxyethyl)-N,N-di(tallow acyloxyethyl)ammonium methosulfate, bis(palmitoyl)ethylhydroxyethylmethylammonium methosulfate or methyl-N,N-bis(acyloxyethyl)-N-(2-hydroxyethyl)ammonium methosulfate. If quaternized compounds of formula (II) that have unsaturated alkyl chains are used, the acyl groups whose corresponding fatty acids have an iodine number between 5 and 25, preferably between 10 and 25 and especially between 15 and 20 and that have a cis/trans isomer ratio (in wt%) of 30:70, preferably greater than 50:50 and especially greater than 70:30, are preferred.

Besides the quaternary compounds described above, it is also possible to use other known compounds, for example quaternary imidazolinium compounds of formula (III)



in which R^7 and R^8 each mean a saturated alkyl residue with 12-18 carbon atoms, R^9 means an alkyl residue with 1-4 carbon atoms or H, and Z means an NH group or oxygen, and A is an anion.

Other suitable quaternary compounds are described by formula (IV)



in which R^{10} stands for a C_{1-4} alkyl, alkenyl or hydroxyalkyl group, R^{11} and R^{12} , independent of one another, represent a C_{8-28} alkyl group, and p is a number between 0 and 5.

Likewise usable are alkylamidoamines, especially fatty acid amidoamines such as the stearylamidopropyldimethylamine that can be obtained under the designation Tego Amid® S 18, as well as the so-called "ester quats," such as the methylhydroxyalkyldialkoxoxyalkylammonium methosulfate sold under the trade name Stepantex® or the products of Cognis Deutschland GmbH that are known as Dehyquart®.

Organic carriers that are especially preferred in accordance with the invention are paraffins and quaternary ammonium compounds.

In addition, it is preferred if the organic carriers have melting or softening points above 40°C and under 100°C, and can be melted without decomposition.

It is understood in the sense of the invention that the nanoparticulate composite material can also comprise two or more organic carriers.

It proved to be particularly advantageous in many cases to use a substance that is otherwise a conventional ingredient in the preferred usage forms of the composite material, namely as a component of washing, rinsing and cleaning agents and cosmetic preparations, as organic carrier for the composite material in many cases.

An aqueous dispersion in the sense of the invention is understood to mean a dispersion whose liquid phase consists of water or a homogeneous mixture with water with one or more nonaqueous polar solvents such as ethanol, glycerol, ethylene glycol, propylene glycol or N-methylpyrrolidone.

To be able to form a dispersion, it is understood that in the sense of the invention only organic carriers and fragrances with a sufficiently low solubility in the liquid phase of the dispersion are suitable. Here the composite material of carrier and fragrance mixture should be sparingly soluble in the liquid phase of the dispersion, where sparing solubility should be

understood to mean a solubility of the components of the nanoparticulate composite materials of less than 5 wt%, preferably less than 1 wt%, with respect to the total weight of the dispersion.

The nanoparticulate composite materials in accordance with the invention are preferably coated with at least one surface modification agent.

Surface modification agents are understood to mean substances that physically adhere to the surface of the nanoparticles, but preferably do not chemically react with it. The individual molecules of the surface modification agent adsorbed on the surface are essentially free of intermolecular bonds to each other. Surface modification agents are to be understood in particular to mean dispersion agents. Dispersion agents are known to the specialist, for example under the terms emulsifiers, protective colloids, wetting agents and detergents.

For example, emulsifiers of the type of the nonionic surfactants from at least one of the following groups are possibilities as surface modification agents:

(1) Addition products of 2-30 mol ethylene oxide and/or 0-5 mol propylene oxide to linear fatty alcohols with 8-22 C atoms, to fatty acids with 12-22 C atoms, and to alkylphenols with 8-15 C atoms in the alkyl group;

(2) C_{12/18} fatty acid monoesters and diesters of addition products of 1-30 mol ethylene oxide to glycerol;

(3) Glycerol monoesters and diesters and sorbitan monoesters and diesters of saturated and unsaturated fatty acids with 6-22 carbon atoms and their ethylene oxide addition products;

(4) Alkyl mono- and oligoglycosides with 8-22 carbon atoms in the alkyl residue and their ethoxylated analogs;

(5) Addition products of 15-60 mol ethylene oxide to castor oil and/or hydrogenated castor oil;

(6) Polyol and especially polyglycerol esters such as polyglycerol polyricinoleate, polyglycerol poly-12-hydroxystearate or polyglycerol dimerate. Likewise suitable are mixtures of compounds of more than one of these classes of substances;

(7) Addition products of 2-15 mol ethylene oxide to castor oil and/or hydrogenated castor oil;

(8) Partial esters based on linear, branched, unsaturated or saturated C_{6/22} fatty acids, ricinolic acid and 12-hydroxystearic acid and glycerol, polyglycerol, pentaerythritol, dipentaerythritol, sugar alcohols (for example, sorbitol), alkyl glucosides (for example, methyl glucoside, butyl glucoside, lauryl glucoside) and polyglucosides (for example, cellulose);

(9) Mono-, di- and trialkyl phosphates and mono-, di- and/or tri-PEG-alkyl phosphates and their salts;

(10) Lanolin alcohols;

- (11) Polysiloxane polyalkyl polyether copolymers and the corresponding derivatives;
- (12) Mixed esters of pentaerythritol, fatty acids, citric acid and fatty alcohols and/or mixed esters of fatty acids with 6-22 carbon atoms, methyl glucose and polyols, preferably glycerol or polyglycerol,
and
- (13) Polyalkylene glycols.

The addition products of ethylene oxide and/or propylene oxide to fatty alcohols, fatty acids, alkyl phenols, glycerol monoesters and diesters and sorbitan monoesters and diesters of fatty acids or to castor oil are known commercially available products. These are homolog mixtures whose average degree of alkoxylation corresponds to the ratio of the amounts of ethylene oxide and/or propylene oxide and substrate with which the addition reaction is carried out.

C_{8/18} alkylmono- and oligoglycosides, their preparation and their use are known from the prior art. Their preparation takes place in particular through the reaction of glucose or oligosaccharides with primary alcohols with 8-18 C atoms. Both monoglycosides in which a cyclic sugar residue is glycosidically linked to the fatty alcohol and oligomeric glycosides with a degree of oligomerization of preferably about 8 are suitable as glycoside residue. The degree of oligomerization is a statistical average value that goes back to the usual homolog distribution for such industrial products.

Typical examples of anionic surfactants and emulsifiers are soaps, alkylbenzene sulfonates, alkane sulfonates, olefin sulfonates, alkyl ether sulfonates, glycerol ether sulfonates, α -methyl ester sulfonates, sulfofatty acids, alkyl sulfates, alkyl ether sulfates such as fatty alcohol ether sulfates, glycerol ether sulfates, hydroxy mixed ether sulfates, monoglyceride (ether) sulfates, fatty acid amide (ether) sulfates, mono- and dialkyl sulfosuccinates, mono- and dialkylsulfosuccinamates, sulfotriglycerides, amide soaps, ether carboxylic acids and their salts, fatty acid isethionates, fatty acid sarcosinates, fatty acid taurides, N-acylamino acids such as acyl glutamate and acyl aspartate, alkyl oligoglucoside sulfates, protein fatty acid condensates (in particular plant products based on wheat), and alkyl (ether) phosphates. If the anionic surfactants contain polyglycol ether chains, these chains can have a conventional homolog distribution, but preferably they have a narrow homolog distribution.

In addition, zwitterionic surfactants can be used as emulsifiers. Surface-active compounds that have at least one quaternary ammonium group and at least one carboxylate and one sulfonate group in the molecule are called zwitterionic surfactants. Especially suitable zwitterionic surfactants are the so-called betaines like the N-alkyl-N,N-dimethylammonium glycinate, for example cocoalkyldimethylammonium glycinate, N-acylaminopropyl-N,N-

dimethylammonium glycinate, for example cocoacylammonopropyl dimethylammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethylimidazolines with 8-18 C atoms in the alkyl or acyl group, and cocoacylaminoethylhydroxyethylcarboxymethyl glycinate. Especially preferred is the fatty acid amide derivative known under the CTFA name cocamidopropyl betaine. Likewise suitable emulsifiers are ampholytic surfactants. Ampholytic surfactants are understood to be those surface-active compounds that contain, besides a $C_{8/18}$ alkyl or acyl group in the molecule, at least one free amino group and at least one $COOH$ - or $-SO_3H$ - group and that are capable of forming internal salts. Examples of suitable ampholytic surfactants are N-alkylglycines, N-alkylpropionic acids, N-alkylaminobutyric acids, N-alkyliminodipropionic acids, N-hydroxyethyl-N-alkylamidopropylglycines, N-alkyltaurines, N-alkylsarcosines, 2-alkylaminopropionic acids and alkylaminoacetic acids with 8-18 C atoms in the alkyl group. Especially preferred ampholytic surfactants are N-cocoalkyl aminopropionate, cocoacylaminoethyl/aminopropionate and $C_{12/18}$ acylsarcosine. Besides the ampholytic emulsifiers, quaternary emulsifiers are also possibilities, with ones of the type of the ester quats, preferably methyl-quaternized difatty acid triethanolamine ester salts, being especially preferred.

Protective colloids that are suitable as surface modification agents are, for example, natural water-soluble polymers such as gelatin, casein, gum arabic, lysalbinic acid, starch, albumin, alginic acid and their alkali and alkaline earth salts, water-soluble derivatives of water-insoluble polymer natural substances such as cellulose ethers like methylcellulose, hydroxyethylcellulose, carboxymethylcellulose or modified carboxymethylcellulose, hydroxyethyl starch or hydroxypropyl guar, as well as synthetic water-soluble polymers such as polyvinyl alcohols, polyvinylbutyrals, polyvinylpyrrolidones, polyalkylene glycols, polyaspartic acids and polyacrylates.

Nonionic surfactants are preferred as surface modification agents, especially alkyl polyglycosides in which the alkyl residue contains between 12 and 16 carbon atoms, fatty alcohol alkoxylates and fatty acid alkanolamides. For the case that the organic carrier is a quaternary compound, only nonionic and/or cationic substances are possibilities as surface modification agents, but not anionic substances such as anionic surfactants. The choice of surface modification agents that are suitable for a certain organic carrier is possible by means of simple routine tests.

The amount of the surface modification agent with respect to the composite material corresponds at least to the amount that is necessary to obtain a stable dispersion of nanoparticles of the composite material. This minimal amount can in each case be determined by simple routine experiments.

As a rule, to produce the nanoparticulate composite material the composite material and the surface modification agent are used in a weight ratio of 1:50 to 50:1, preferably 1:5 to 10:1 and especially 1:2 to 2:1. Instead of the given amounts of surface modification agent it is also possible to use a mixture of two or more surface modification agents in the same amount.

The dispersions of nanoparticulate composite materials in accordance with the invention can be prepared in the teaching of the melt emulsification method that is known, for example, from EP-B1 0 506 197 for preparation of nanoparticulate wax dispersions where in one possible variation of the method

(a) a melt of the organic carrier with a minimum of one fragrance is prepared, optionally in the presence of a surface modification agent,

(b) this melt is dispersed in a liquid, preferably water, with which the melt is not miscible, and

(c) the temperature is then cooled below the melting point of the mixture of carrier, fragrance(s) and optionally surface-modification agent.

In the preferred embodiment of the preparation method the fragrance mixture is first heated together with the organic carrier material until a liquid phase arises. Then one or more surface modification agents are added and the mixture is mixed until a homogeneous liquid phase has formed. If necessary, it is additionally heated for this. Then water is added to the mixture, which is immiscible with water, while stirring and with the formation of a microemulsion; the water had been previously heated to a temperature that is above the melting point of the mixture of fragrance mixture, organic carrier material, and optional surface modification agents. The microemulsion is then slowly cooled to solidify the microemulsified particles, which expediently takes place while stirring, and a stable dispersion of the nanoparticulate composite materials is formed.

Another object of the invention is thus a method for preparing an aqueous dispersion of a nanoparticulate composite material, where the composite material comprises at least one fragrance and an organic carrier and the particles have an average particle diameter in the range of 1-500 nm, in which

(a) the molten organic carrier is emulsified with the fragrance, optionally in the presence of a surface modification agent, and

(b) the emulsion is cooled to a temperature below 40°C.

Furthermore, variations of this method that lead to the desired dispersions in the same way are possible. For example, in the first step of the method the surface modification agent(s) can be heated together with the organic carrier material and the fragrance mixture up to the formation of a homogeneous liquid phase right from the start. In another variation of the

preparation method the heated water can be present and the liquid phase of fragrance mixture, organic carrier material, and optional surface modification agents can be added to the water.

Of course, in each case one should operate at temperatures that are as low as possible in order to avoid losses of the volatile fragrances. Preferably, however, fragrance mixtures are used with which evaporation losses are so low that they do not adversely affect the odor profile of the composite materials in the course of the preparation process of the composite materials in accordance with the invention. According to the findings of the inventors, it is, however, possible in accordance with the teaching of the invention to convert such fragrance mixtures to composite materials in accordance with the invention that contain fragrance components with a boiling point under the maximum working temperature of the said preparation process. If especially low boiling fragrances are to be used, it can be expedient to add suitable auxiliary substances to reduce the melting point of the mixture of fragrance mixture, organic carrier material and optional surface modification agents.

Instead of water, it is also possible in accordance with the invention to use mixtures of water and nonaqueous polar solvents such as ethanol, glycerol, ethylene glycol, propylene glycol or N-methylpyrrolidone, provided the nanoparticulate composite materials are sparingly soluble in these aqueous mixtures, where the term "sparing solubility" is defined as above.

The dispersions of nanoparticulate composite materials prepared by the method in accordance with the invention are characterized by high storage stability.

The composite material, optionally together with the surface modification agent, should be capable of producing stably dispersible nanoparticles in water or aqueous mixtures in accordance with the above described preparation process, where the average particle diameter of the nanoparticles lies in the range of 1-500 nm. The organic carrier substances that can be used and the optional additionally necessary surface modifications can be chosen by simple routine experiments.

The preparation process that was mentioned is to be understood merely as an example and does not represent any restriction.

The dispersions in accordance with the invention can contain between 1 and 60 wt% of the nanoparticulate composite materials and/or between 0.1 and 10 wt% of the fragrance or fragrance mixture, in each case with respect to the total weight of the dispersion.

It was found that the release of fragrance in the fragrances present in the composite materials in accordance with the invention is clearly delayed in time compared to the otherwise identical fragrances that are present in free form. This means that fragrance released from the composite material persists considerably longer. As far as the fragrance intensity over the course of time goes, it is considerably more uniform with the composite materials in accordance with

the invention. While the fragrance intensity of the fragrances in free form is high at the start and then rapidly falls off, the fragrance intensity of the composite material in accordance with the invention is indeed lower at the start than with the free fragrance, but it then stays at a clearly higher level over a longer time.

It is assumed that the fragrances in the composite materials in accordance with the invention can be present, for example, in the form of solid solutions, enclosed in small hollows of the carrier or even partially adsorbed on the particle surface. The release of fragrances contained within the particles can take place through diffusion to the surface. However, it is also possible to release all of the contained fragrances over a very short time by heating the composite materials above their melting point and thereby to bring about a nearly instant release of the odor that is connected with the fragrances. Accordingly, the fragrance mixture that is contained in the composite materials can be released from the composite materials in accordance with the invention in a controlled way.

In each case according to the fragrance mixture that is used the odor characteristic of the composite material in accordance with the invention can correspond or even deviate from that of the free fragrance mixture. However, through the appropriate choice of the fragrances contained in the mixture and their concentration in the fragrance mixture the specialist can always establish the desired odor impression for the composite material in accordance with the invention.

It was found that nanoparticulate composite materials that adhere especially well to substrates and in particular to the surfaces of substrates, i.e., that have a particularly high substantivity, can be prepared by the teaching of the invention. This applies in particular to textile fibers and keratin fibers such as human hair, but surfaces in the sense of the invention are also understood to mean, for examples, surfaces of hard substrates such as ceramic fibers, glass, floors or the surfaces of furniture, or other objects.

With that it is possible to confer a long-lasting odor to substrates and in particular the surfaces of substrates with the nanoparticulate composite materials in accordance with the invention.

Accordingly, another object of this invention is the use of an aqueous dispersion of a nanoparticulate composite material, where the composite material comprises at least one fragrance and an organic carrier and the particles have an average particle diameter in the range of 1-500 nm, for perfuming a substrate, in particular a textile, a keratin fiber or a hard surface.

The aqueous dispersions of nanoparticulate composite materials in accordance with the invention can be stably incorporated into formulations, even if they contain a high amount of water, and with that can enable higher usage concentrations of fragrances than with the use of the free fragrances.

The invention additionally comprises the use of an aqueous dispersion of a nanoparticulate composite material, where the composite material consists of at least one fragrance and an organic carrier and the particles have an average particle diameter in the range of 1-500 nm, in washing, rinsing, cleaning and finishing preparations and in cosmetic preparations. It was specifically found that the task of transferring a long lasting odor to the objects or to the human body or parts thereof that have been treated with these preparations can be solved through the use of washing, rinsing, cleaning or finishing preparations and cosmetic preparations, when dispersions of nanoparticulate composite materials in accordance with this invention are used in the relevant preparations.

Another object of this invention accordingly consists of preparations consisting of an aqueous dispersion of a nanoparticulate composite material, where the composite material contains at least one fragrance and an organic carrier and the particles have an average particle diameter in the range of 1-500 nm, besides the usual components of a washing agent preparation in the case of washing agents, besides the usual components of a rinsing agent preparation in the case of rinsing agents, besides the usual components of a cleaning agent preparation in the case of cleaning agents, besides the usual components of a finishing agent preparation in the case of finishing agents, and besides the usual components of a cosmetic preparation in the case of cosmetic preparations. Preferred preparations are aqueous preparations.

Additionally preferred are liquid washing agents, finishing agents such as laundry softeners and spray starches.

Washing, rinsing, cleaning and finishing agent preparations contain as active substances substances like surfactants (anionic, nonionic, cationic and amphoteric surfactants), builder substances (inorganic and organic builders), bleaches (for example, peroxy bleaches and chlorine bleaches), bleach activators, bleach stabilizers, bleach catalysts, enzymes, particular polymers (for example, ones with cobuilder properties), antiredeposition agents, dyes and odorants (perfumes), without the ingredients being restricted to these groups of substances. Frequently, important ingredients of these preparations are also detergent aids and cleaning aids, for which one may mention as examples and in a nonrestricting fashion optical brighteners, UV protective substances, soil repellents, thus polymers that counteract the redeposition of fibers or hard surfaces, and silver protection agents.

In a preferred embodiment the cosmetic preparations are aqueous preparations that are especially suitable for treatment of keratin fibers, in particular human hair, or for treatment of human skin. The hair treatment agents are in particular agents for treatment of human scalp hair. The agents that are especially preferred in accordance with the invention include hair washing agents and hair care agents like hair shampoos, hair rinses and hair cures.

One cosmetic preparation that is likewise preferred in accordance with the invention is a deodorant spray.

To prepare the said preparations, the aqueous dispersion of a nanoparticulate composite material in accordance with the invention, optionally after prior dilution with water, for example, is preferably mixed or dispersed with the other recipe components in a substantially known way at a temperature under the melting point of the composite material.

In the said preparations the dispersions in accordance with the invention are used in an amount such that the nanoparticulate composite material is contained in an amount in the range from 0.01-30 wt%, preferably in an amount in the range from 0.1-10 wt%, and especially in an amount in the range from 0.5-2 wt%, with respect to the total weight of the preparation. In the case of fabric softeners the preferred usage concentration of the nanoparticulate composite material is in the range of 0.1-30 wt%, and for hair rinses it is in the range of 0.1-20 wt%, in each case with respect to the total weight of the preparation.

Likewise, an object of the invention is a method for perfuming a substrate, in which the surface of the substrate is brought into contact with an amount of a dispersion in accordance with the invention, as described above, or a preparation, as described above, in an amount that is olfactorally effective.

The invention also concerns washing processes, in particular for machine washing of laundry, rinsing processes, especially for machine dishwashing, cleaning processes, especially for cleaning surfaces or objects, and finishing processes especially for textiles, in which preparations in accordance with the invention are applied in the relevant aqueous baths and the substrates are treated with the baths containing the preparations. The treatment in this case can also take place by spraying the object with the preparation or the bath.

The invention also concerns a cosmetic treatment process in which a cosmetic preparation in accordance with the invention is brought in contact with the human body or a part thereof and thus cosmetically treats said body or part of the body.

The following examples are intended to illustrate this invention without limiting it. All percentage data, unless otherwise indicated, refer to the total weight of the preparation.

Examples

A perfume oil of the following composition was used for Examples 1-6 in accordance with the invention:

	Fragrance	Amount in wt%
	Dihydromyrcenol	5.50
	Aldehyde C 12	0.40
	Aldehyde C 12. MNA	0.20
	Alcohol C 10	0.50
	Cyclovertal	0.50
	Phenylacetaldehyde dimethyl acetal	0.50
	Herbavert	1.00
	Undecavertol	0.50
	Allyl caproate	0.50
	Aldehyde C 14 sog	0.50
	Melusate	1.00
	Ortho-tert-butylcyclohexyl acetate	1.20
	Aldehyde C 16 sog	0.50
	Frambinone methyl ether	1.00
	Benzyl acetone	2.50
	Acedyl	5.00
	Isobornyl acetate	5.00
	Styrollyl acetate	1.00
	Troenan	2.50
	Citronellol	2.50
	Tetrahydrolinalool	3.00
	Diphenyl ether	0.70
	Hedione	2.50
	Ionone	6.00
	Cyclohexyl salicylate	22.50
	Iso E Super	20.50
	Coumarin	0.50
	Galaxolide 50	12.00
	Total	100.00

Example 1 in accordance with the invention: Preparation of a nanoparticulate dispersion of a composite material of paraffin and perfume oil

3 g perfume oil was dissolved in 100 g molten paraffin (aliphatic C15 hydrocarbons) and 100 g Mergital B10 (behenyl alcohol with 10 EO) at 90°C. Then 150 g water that had been preheated to 90°C was added by drops with the formation of an opalescent liquid, and it was

stirred further for 30 min at 90°C. Then another 150 g water at 90°C was added, with the formation of a milky viscous dispersion, which was stirred for another 5 min at 90°C, and then cooled to room temperature. The particle size distribution determined by light scattering showed particle sizes between 30 and 120 nm with a peak at 100 nm.

Example 2 in accordance with the invention: Preparation of a nanoparticulate dispersion of a composite material of paraffin and perfume oil

0.5 g perfume oil was dissolved in 20 g molten paraffin (aliphatic C15 hydrocarbons) at 90°C, then 20 g Mergital B 10 was added while stirring and stirred for another 5 min. Then 30 g 90°C water was slowly added by drops with the formation of an opalescent gel. Then another 29.5 g at 90°C was rapidly added, stirred for about 15 min, and then slowly cooled to room temperature with the formation of a stable white suspension. This suspension could be diluted to an opalescent solution with water. The particle size distribution gave a volume-weighted average value of 31 nm.

Example 3 in accordance with the invention: Preparation of a nanoparticulate dispersion of a composite material of paraffin and perfume oil

0.5 g perfume oil was dissolved in 20 g molten paraffin (aliphatic C15 hydrocarbons) at 90°C, then 20 g Mergital B 10 was added while stirring, and stirred for another 5 min. Then 59.5 g 90°C water was slowly added by drops with the formation of an opalescent gel. It was stirred for about 15 min and then slowly cooled to room temperature with the formation of a stable white dispersion. After dilution with water a particle size distribution by light scattering showed a volume-weighted particle size of 15 nm.

Example 4 in accordance with the invention: Preparation of a nanoparticulate dispersion of a composite material of a quaternary ammonium compound and perfume oil

1 g perfume oil was dissolved in 20 g Dehyquart AU 56 (dipalmitoylethyl hydroxyethyl methylammonium methosulfate) at 85°C. Then 20 g Plantacare 1200 UP (C12-C16 alkyl polyglycoside) was added while stirring and stirred for 5 min. Then this mixture was added to 55 g water at 85°C and then heated to 90°C while continuing to stir and stirred at this temperature for 30 min. Then the temperature was slowly lowered to room temperature. A milky white creamy stable dispersion was obtained. The average particle size was found to be 300 nm.

Example 5 in accordance with the invention: Preparation of a nanoparticulate dispersion of a composite material of a quaternary ammonium compound and perfume oil

1 g perfume oil was dissolved in 20 g Dehyquart AU 56 at 80°C. Then 10 g Genapol T 500 (C16-C18 fatty alcohol + 50 EO) was added while stirring and stirred for 5 min. Then this mixture was added by drops to 69 g water at 85°C and then while continuing to stir heated to 90°C and stirred at this temperature for 30 min. Then the temperature was slowly lowered to room temperature. A creamy dispersion was obtained. The average particle size was found to be 150 nm.

Comparison Example 6: Preparation of a nanoparticulate dispersion of a quaternary ammonium compound with an additional content of perfume oil

20 g Dehyquart AU 56 was melted together with 3 g Genapol T 500 at 100°C while stirring. Then this mixture was added by drops to 76 g 85°C water and then, while continuing to stir, heated to 90°C and stirred at this temperature for 30 min. Then the temperature was slowly lowered to room temperature, after which 1 g perfume oil was stirred in and stirred for another 5 min. A dilute dispersion was obtained. The average particle size was found to 150 nm.

Example 7: Determination of release kinetics of fragrances

In a model experiment the release kinetics of individual fragrances from the dispersion of Example 5 in accordance with the invention in comparison with the conventionally prepared dispersion from Comparison Example 6, in which the perfume was present in free form, i.e., not as a component of a composite material, was investigated. For this equal samples of the two dispersions were applied to filter paper strips and these were then stored at room temperature for 1 h or 3 h. After the storage times the paper strips were put into a headspace apparatus and thermostatted there at 45°C for 15 min. The fragrances then found in the vapor space, Herbavert, dihydromyrcenol, tetrahydrolinalool and isobornyl acetate, were identified by means of GC/MS coupling and spectral comparison using a substance library, and in parallel quantified by means of an FID. The numerical values given in the following table represent relative peak areas and are a measure of the concentration of the relevant fragrance.

Fragrance (in parentheses: measurement time)	Example 5 in accordance with the invention	Comparison Example 6
Herbavert (1 h)	580	180
Herbavert (3 h)	27	5
Dihydromyrcenol (1 h)	780	260
Dihydromyrcenol (3 h)	170	56
Tetrahydrolinalool (1 h)	360	130
Tetrahydrolinalool (3 h)	36	28
Isobornyl acetate (1 h)	360	90
Isobornyl acetate (3 h)	39	4

These results show that in all cases the dispersion in accordance with the invention led to a considerably higher concentration of fragrance in the gas space after 1 or 3 h. This higher concentration in the gas space correlates directly with the correspondingly higher odor intensity. One can likewise see directly from the results that in the case of the Comparison Example 6 the primary amount of the fragrances had already become volatile in the course of the first hour of the experiment.

It should be particularly noted that even in the case of the more volatile fragrance Herbavert the dispersion in accordance with the invention led to a considerably higher concentration of fragrance in the gas phase after 1 and 3 h, even though in this case the fragrance mixture had been heated to 90°C in the course of the preparation of the dispersion, while this was not the case in the comparison example.

Claims

1. An aqueous dispersion of a nanoparticulate composite material, where the composite material consists of at least one fragrance and an organic carrier and the particles have an average particle diameter in the range of 1-500 nm.
2. A dispersion as in Claim 1, which is characterized by the fact that the organic carrier is chosen from the group that is formed by waxes, higher fatty alcohols, fatty alcohol alkoxylates, fatty acid amides, quaternary ammonium compounds, and quaternary phosphonium compounds.
3. A dispersion as in Claim 2, which is characterized by the fact that the organic carrier is a paraffin.
4. A dispersion as in Claim 2, which is characterized by the fact that the organic carrier is a quaternary ammonium compound.
5. A dispersion as in one of Claims 1-4, which is characterized by the fact that the organic carrier can be melted without decomposition at a temperature between 40 and 100°C.

6. A dispersion as in one of Claims 1-5, which is characterized by the fact that the minimum of one fragrance is a perfume oil.

7. A dispersion as in one of Claims 1-6, which is characterized by the fact that the particles are coated by at least one surface modification agent.

8. A dispersion as in Claim 8 [sic], which is characterized by the fact that the minimum of one surface modification agent is chosen from the group that is formed by the nonionic surfactants.

9. A dispersion as in Claim 9 [sic], which is characterized by the fact that the minimum of surface modification agent is an alkyl polyglycoside and/or a fatty alcohol alkoxylate.

10. A dispersion as in one of Claims 1-9, which is characterized by the fact that it contains between 1 and 60 wt% of the nanoparticulate composite material, with respect to the total weight of the dispersion.

11. A dispersion as in one of Claims 1-9, which is characterized by the fact that it contains between 0.1 and 10 wt% of the fragrance or fragrance mixture, with respect to the total weight of the dispersion.

12. A method for producing a dispersion as in one of Claims 1-11, in which
(a) the molten organic carrier is emulsified with the fragrance, optionally in the presence of a surface modification agent, in water and

(b) the emulsion is cooled to a temperature under 40°C.

13. The use of a dispersion as in one of Claims 1-11 for controlled release of at least one fragrance.

14. The use of a dispersion as in one of Claims 1-11 to perfume a substrate.

15. A use as in Claim 14, which is characterized by the fact that the substrate is a textile, a keratin fiber, or a hard surface.

16. A preparation that consists of, besides the usual components of a washing agent preparation, a dispersion as in one of Claims 1-11.

17. A preparation that consists of, besides the usual components of a rinsing agent preparation, a dispersion as in one of Claims 1-11.

18. A preparation that consists of, besides the usual components of a cleaning agent preparation, a dispersion as in one of Claims 1-11.

19. A preparation that consists of, besides the usual components of a finishing agent preparation, a dispersion as in one of Claims 1-11.

20. A preparation that consists of, besides the usual components of a cosmetic preparation, a dispersion as in one of Claims 1-11.

21. A preparation as in one of Claims 16-20, which is characterized by the fact that the nanoparticulate composite material is contained in the preparation in an amount in the range of 0.01-30 wt%, preferably in an amount in the range of 0.1-10 wt%, and especially in an amount in the range of 0.5-2 wt%, with respect to the total weight of the preparation.

22. A method for perfuming a substrate, in which the surface of the substrate is brought into contact with an olfactorally active amount of a dispersion as in one of Claims 1-11 or a preparation as in one of Claims 16-20.

23. A washing method, in particular a method for machine laundering, in which a preparation as in Claim 16 is applied to the wash water and the laundry material is treated with it.

24. A rinse method, especially a method for machine dishwashing, in which a preparation as in Claim 17 is applied to the rinse [wash] water and the items to be rinsed [washed] is treated therewith.

25. A cleaning method for cleaning surfaces or objects, in which a preparation as in Claim 18 is applied to the cleaning water and the surface or the object is treated therewith.

26. A finishing method for textiles, in which a preparation as in Claim 19 is applied to the wash water or finishing water and the textiles are treated therewith.

27. A cosmetic treatment method in which a preparation as in Claim 20 is brought into contact with the human body or a part thereof and thus this part is cosmetically treated.

INTERNATIONAL SEARCH REPORT

 Inte Application No
 PCT/EP 01/14639

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D3/50 A61K7/46 A61L9/01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D A61K A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 27 47 726 A (PROCTER & GAMBLE) 3 May 1978 (1978-05-03) page 4; claims	1-6, 10, 17-23, 26
X	EP 0 447 318 A (OREAL) 18 September 1991 (1991-09-18) page 2; claims page 4	1, 3-8, 10, 11, 13, 14, 16-20, 22, 27
X	WO 00 68352 A (UNILEVER PLC ; LEVER HINDUSTAN LTD ; UNILEVER NV) 16 November 2000 (2000-11-16) claims; examples	1, 5, 6, 10, 11, 13, 16-19, 21-26
-/-		

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

Z document member of the same patent family

Date of the actual completion of the international search

24 April 2002

Date of mailing of the international search report

03/05/2002

Name and mailing address of the ISA

 European Patent Office, P.B. 5818 Patentleer 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 681 epo nl
 Fax: (+31-70) 340-3016

Authorized officer

Pfannenstein, H

INTERNATIONAL SEARCH REPORT

 Int. Application No.
 PCT/EP 01/14639

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 346 034 A (UNILEVER PLC; UNILEVER NV) 13 December 1989 (1989-12-13) page 4, line 40; claims page 13	1-3, 5, 6, 10-13, 16-19, 21-26
A	EP 0 466 236 A (QUEST INT) 15 January 1992 (1992-01-15) page 7; claims; examples	1
P, X	EP 1 146 057 A (GIVAUDAN SA) 17 October 2001 (2001-10-17) page 4; claims page 10	1, 6, 7, 10, 11, 13-20

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No.
PCT/EP 01/14639

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 2747726	A	03-05-1978	GB 1587122 A	01-04-1981
			AU 520108 B2	14-01-1982
			AU 3013877 A	03-05-1979
			CA 1111616 A1	03-11-1981
			DE 2747726 A1	03-05-1978
			FR 2369340 A1	26-05-1978
			GR 62860 A1	06-07-1979
			IT 1143767 B	22-10-1986
			JP 53094042 A	17-08-1978
			US 4152272 A	01-05-1979
EP 0447318	A	18-09-1991	FR 2659554 A1	20-09-1991
			AT 123219 T	15-06-1995
			CA 2038331 A1	17-09-1991
			DE 69110070 D1	06-07-1995
			DE 69110070 T2	12-10-1995
			DK 447318 T3	02-10-1995
			EP 0447318 A1	18-09-1991
			ES 2072563 T3	16-07-1995
			JP 2676281 B2	12-11-1997
			JP 5148129 A	15-06-1993
			US 6203802 B1	20-03-2001
			US 2001010824 A1	02-08-2001
			ZA 9101933 A	24-12-1991
WO 0068352	A	16-11-2000	AU 4548000 A	21-11-2000
			BR 0010307 A	26-02-2002
			WO 0068352 A1	16-11-2000
			EP 1175484 A1	30-01-2002
EP 0346034	A	13-12-1989	US 4919841 A	24-04-1990
			AU 623143 B2	07-05-1992
			AU 3600589 A	07-12-1989
			BR 8902601 A	23-01-1990
			DE 68914334 D1	11-05-1994
			DE 68914334 T2	28-07-1994
			EP 0346034 A2	13-12-1989
			ES 2051358 T3	16-06-1994
			JP 2035935 A	06-02-1990
			JP 6051112 B	06-07-1994
			ZA 8904273 A	27-02-1991
EP 0466236	A	15-01-1992	AT 109963 T	15-09-1994
			DE 69103487 D1	22-09-1994
			DE 69103487 T2	16-02-1995
			EP 0466236 A1	15-01-1992
			JP 2514124 B2	10-07-1996
			JP 5201845 A	10-08-1993
			US 5334581 A	02-08-1994
			US 5190915 A	02-03-1993
			US 5246918 A	21-09-1993
			ZA 9105406 A	31-03-1993
EP 1146057	A	17-10-2001	EP 1146057 A1	17-10-2001
			AU 6384301 A	30-10-2001
			WO 0179303 A1	25-10-2001